



Bimetallic Ru–Cu as a highly active, selective and stable catalyst for catalytic wet oxidation of aqueous ammonia to nitrogen



Jile Fu^a, Kaixu Yang^a, Changjian Ma^a, Nouwei Zhang^{a,*}, Hengjun Gai^b, Jinbao Zheng^a, Bing H. Chen^{a,*}

^a Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, Xiamen University, Xiamen 361005, PR China

^b Qingdao University of Science and Technology, Shandong, Qingdao 266042, China

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ABSTRACT

Ru/C, Cu/C and bimetallic Ru–Cu/C catalysts are prepared via chemical reduction methods and investigated for catalytic wet oxidation of aqueous ammonia to nitrogen. It is found that the as-prepared bimetallic Ru–Cu/C catalyst is very active and selective as well stable as for selective oxidation of aqueous ammonia toward nitrogen at rather mild conditions. The results show that the Ru–Cu/C catalyst is much more efficient especially stable than the corresponding monometallic Ru/C and Cu/C catalysts, indicating the synergistic effect of Cu and Ru. These catalysts are characterized by XRD, XPS, TEM, and H₂-TPR, and the results are revealed that there is strong interaction between Ru and Cu over Ru–Cu/C catalysts and the co-presence of Ru and Cu can effectively adjust the reactivity and converge of oxygen species as well as protect the Ru and Cu from leaching. The strong interaction, synergistic effect, proper oxygen nature and ability against leaching could be attributed to the excellent catalytic property of Ru–Cu/C catalyst.

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1. Introduction

Ammonia in wastewater not only causes serious eutrophication problems but also has toxic and harmful effects on aquatic life and human beings. With the increasing environmental concerns, the abatement of aqueous ammonia has become a critical issue. Conventionally, biological and chemical treatment processes are adopted [1–5] to convert it to harmless nitrogen. Compared with these traditional methods, catalytic wet air oxidation (CWAO) is a much more efficient and environmental-friendly technology for ammonia wastewater treatment [6], in which ammonia can be directly and selectively converted to N₂ over proper catalysts.

Various types of catalytic materials have been investigated for catalytic wet oxidation of aqueous ammonia to N₂. Among these materials, noble metals such as Ru, Pd and Pt, were widely used as active catalysts due to their superior catalytic performance. Qin et al. obtained 99% ammonia removal with 2 g of Pd or Ru (3 wt%)/Al₂O₃ catalyst for 100 mL of ammonium chloride solution (NH₃: 1695 mg/L, pH 12.3) at 230 °C in a batch reactor, in which both

Pd and Ru/Al₂O₃ can convert 99% ammonia to N₂ at 230 °C with the addition of NaOH in order to adjust the pH [7]. In another work [8], Pt/TiO₂ catalyst could completely convert NH₄⁺ to N₂ at 200 °C and 36 bar of air. However, clearly the works on reported literature using precious metal catalysts can only be worked under rather severe conditions (temperature >150 °C and/or pressure >1.0 MPa) and the metal loading is usually as high as 3 wt% (as listed in Table 1), these limit their pave toward industrial applications. Transition metal based catalysts were also utilized due to much lower cost although they are usually at the same time much lower activity than precious metals. Using transition metal alone, e.g., a Ni/Al₂O₃ catalyst, only 21% of ammonia was removed even at 230 °C and 2.0 MPa [9]. Co/Ce, Mn/Ce composite oxides [10] and Mn, Co, Mo, Fe, Cr supported on activated carbon [11] or Al₂O₃ [12] have also been used in the CWAO of ammonia. The results show that these catalysts have no activity when reaction temperature below 250 °C, which further confirms the necessity of noble metals in the CWAO of ammonia if low reaction temperature is required. In order to reduce the costs of catalyst and operation to make the CWAO processes economical feasible and sustainable, more effective catalysts which can work under relative mild reaction conditions at the same time with precious metal loadings as less as possible are urgently needed. However, preparing such catalysts is a very challenging work.

* Corresponding authors.

E-mail addresses: zhnw@xmu.edu.cn (N. Zhang), chenbh@xmu.edu.cn (B.H. Chen).

Based on the reported research works, the oxidizing capability of catalyst plays the crucial role to determine the catalytic performance to convert ammonia to nitrogen via CWAQ. Proper oxygen species is necessary not only for activation of ammonia but also for selective oxidation of ammonia to nitrogen, instead of nitrite and nitrate ions. Qin et al. reported that only those metals including Pd and Ru with moderate oxygen affinity can become the good catalysts for the CWAQ of ammonia [7]. Similarly, Lousteau et al. studied Pt, Pd, Ir, Rh and Ru supported catalysts in the CWAQ of ammonia [13] and established the relationship between the oxygen coverage at the catalyst surface and the catalytic performance, concluding that only the catalysts with appropriate values of metal oxygen bond energy had optimal activity and N₂ selectivity. Generally, surface oxygen over noble metals exhibit higher reaction activity than that over transition metals while transition metals present higher surface oxygen concentration than noble metals. It is reasonable to infer that the activity and concentration of the surface oxygen may be tuned by the coexisting of precious and transition metals if the structure is carefully designed. In fact, transition metals (Fe, Co, Ni, Cu et al) have often been used as promoters to enhance catalytic performances of noble metal catalysts for the reactions involving oxygen activation [14]. Our previous works also revealed that transition metal can tune Pt-based catalyst's oxophilicity (playing a role in maneuvering surface oxygenated species) and thus the catalytic performance of CO oxidation reaction [15,16]. Therefore, it can be expected that the combination of precious and transition metals would adjust the oxidizing capacity of surface oxygen and thus result in much better catalytic performance for CWAQ ammonia to nitrogen while significantly reducing the use of noble metals in the catalysts. However, for the best of our knowledge, there is virtually no such a report on the application of bimetallic catalysts for CWAQ of ammonia to nitrogen. As can also be seen in Table 1, the CWAQ catalysts used in literature either one noble or transition metal, or bi-noble metals or bi-transition metals, but never use of noble-transition metals together. Furthermore, it is hardly to find reported literature on catalyst stability in CWAQ of ammonia.

It was reported that supported-Ru catalyst presented excellent catalytic performance for CWAQ of ammonia to N₂ [7,13,17]. For the transition metals, Cu is one of the most prospective species to compete with noble metals for CWAQ [6]. Therefore, in this paper, Ru and Cu are combined to adjust the surface oxygen property with the purpose of obtaining more efficient and stable catalysts with much lower Ru loading for catalytic wet air oxidation of ammonia to nitrogen, and Ru/C and Cu/C monometallic catalysts were also studied for comparison. The results indicated that Ru–Cu/C bimetallic catalyst exhibited excellent catalytic performance under relative mild conditions. Characterizations including XRD, H₂ temperature-programmed reduction (H₂-TPR), XPS and TEM were performed to discover the relationship between the catalytic performance and physicochemical properties.

2. Experimental

2.1. Catalyst preparation

Ru–Cu bimetallic catalysts were prepared by a chemical reduction method, using CuCl₂•2H₂O, RuCl₃•3H₂O and BP2000 as active metal precursors and support, respectively. Typically, 0.5 g BP2000 was added into 150 mL solution of CuCl₂•2H₂O (containing the desired Cu). After adjusting the pH to 10 by ammonia, the mixture was stirred for 3.5 h at room temperature. Then desired hydrazine was added to reduce Cu²⁺ to Cu. Two hours later, the 7.65 mL solution of RuCl₃•3H₂O (containing the desired Ru) was added to the mixture. It is worth to point out that ammonia concentration is insufficient for the complexation of cupric ions if pH in the solution is lower than 8, and cuprous oxide, which will weaken the interaction between Cu and Ru, will be produced. After stirring 16 h at room temperature, the mixture was filtered and washed by deionized water. The resultant solid was dried at 60 °C for 24 h. Finally, the solid was calcined in a flow of pure H₂ at 250 °C for 4 h. The obtained catalyst was denoted as xRu–yCu/C, where x and y refer to the mass percent of Ru and Cu. 3Ru/C and 3Cu/C catalysts were prepared by a similar procedure but only Ru or Cu metal precursor was added.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained with a Panalytical X'pert Pro diffractometer operated at 40 kV and 30 mV, using Cu K α radiation. The images of TEM were gained on a Tecnai F30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV. X-ray photoelectron spectra (XPS) were recorded on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K α radiation (1846.6 eV) as the X-ray source. The metal leaching was measured by inductively coupled plasma mass spectrometry (ICP-MS).

For H₂-temperature programmed reduction (TPR), 50.0 mg sample was placed in a quartz reactor as a shallow packed bed, heated in a pure O₂ at 150 °C for 2 h and cooled down to room temperature. After the gas was switched to 7.0% H₂/Ar, the temperature was increased to 400 °C at the rate of with 10 °C/min.

2.3. Apparatus and procedure

The reaction procedure in this work is similar to Lee's work [24]. The difference is that the total volume of the reactor was 100 mL. Generally 0.5 g catalyst and 50 mL solution with 1000 ppm ammonia were added into the reactor for every reaction through this paper. All reactions were carried out in a stainless steel reactor with 100 mL capacity volume and a magnetic spin bar was used for stirring. The reactor was coated with Teflon liner 2 mm thick inside to avoid corrosion of the reactor wall. The pH of the

Table 1
Summary of reported studies on CWAQ of ammonia to N₂.

Catalyst	Metal loading	Reaction condition	Reference
Ru, Pd supported on Al ₂ O ₃	3%	200–230 °C, 1.5 MPa of O ₂	[7]
Ru/TiO ₂	3%	200 °C, 0.5 MPa of O ₂	[17]
Pt/TiO ₂ , Pt/ZrO ₂	3%	200 °C, 5.0 MPa of air	[8]
Pt, Ru, Pd, and Ru–Pd on CeO ₂	5% for Ru and Pd, 10% for Pt	120–230 °C, 2.0 MPa of O ₂	[18]
Pt–Pd–Rh composite washcoated on γ -Al ₂ O ₃	6.4%	150–230 °C, 2.0 MPa of O ₂	[19]
Pt, Pd, Ru, Rh, Ir supported on TiO ₂ and ZrO ₂	2.5%–3%	200 °C, 5.0 MPa total pressure	[13]
Cu–La–Ce composite coated on cordierite	15%–50%	150–200 °C, 3.0 MPa of O ₂	[20]
Cu/ACF	15%–25%	150–190 °C, 3.0 MPa of O ₂	[21]
Cu/ACF	15%–25%	150–190 °C, 2.0–5.0 MPa of O ₂	[22]
Co-precipitated transition metal–aluminium catalyst (transition metal: Cu, Ni, Co, Fe, and Mn)	No support	230 °C, 2.0 MPa of air	[23]
Ni/Al ₂ O ₃	20%	230 °C, 2.0 MPa of air	[9]
Cu, Co, Mo, Mn, Ru	3%–7%	200 °C, 0.42 MPa of O ₂	[11]

ammonia solution was adjusted by 2 M NaOH solution. After sealing the cover of the reactor, the ambient was purged with O₂ by repeating the filling of pure O₂ at 5 bar followed by venting out, the N₂ present in the reactor was analyzed to be negligible. Thereafter, the reactor was heated to a desired reaction temperature and the pressure was adjusted to the desired value by adding O₂ with a stirring rate of 1400 rpm using a magnetic bar, from which the reaction was started. When the set reaction time was reached, the reactor was moved out from the heating bath and immediately quenched in a ice-water bath to bring temperature of the reaction system to room temperature. Then the gaseous products of the reaction were vented to a collection bag and analyzed by a GC equipped with two columns (Porapak T and Molsieve 5A). The liquid sample from the reactor was collected and filtered and the ammonia-nitrogen was measured by Napierian reagent colorimetric method (GBZ50005–87). The products of further oxidation of ammonia (NO₂[−] and NO₃[−]) were analyzed by HPLC.

As the detected nitrogen containing compounds were only N₂, NH₃, NH₄⁺, NO₃[−], and NO₂, the conversion of ammonia (X_{NH_3}) and selectivity of N₂ (S_{N_2}) can be calculated by the following formulae:

$$X_{\text{NH}_3}(\%) = \frac{C_{\text{NH}_3}^0 - C_{\text{NH}_3}}{C_{\text{NH}_3}^0} \times 100\%$$

$$S_{\text{N}_2}(\%) = \left(1 - \frac{C_{\text{NO}_3^-} + C_{\text{NO}_2^-}}{C_{\text{NH}_3}^0 - C_{\text{NH}_3}} \right) \times 100\%$$

where C^0 is the initial concentration of the substrate in the solution, and C is its current concentration, while the subscripts denote the individual compounds or ions.

3. Results and discussion

3.1. Bimetal effect on the catalytic performance

Bimetallic catalysts usually exhibit special catalytic performance due to the interaction and synergetic effect between different active metals. Cu/C, Ru/C and Ru–Cu/C catalysts with the same total metal loading (3 wt%) were prepared and tested for catalytic wet air oxidation of ammonia to nitrogen.

In order to distinguish the proportion of reaction and adsorption regarding to the decrease of ammonia in wastewater, blank experiments were done for ammonia adsorption of these materials. Our experimental results showed that less than 15% ammonia would be adsorbed by these materials at room temperature for fresh catalyst material. On the other hand, ammonia could not be adsorbed by these materials at reaction temperature (150 °C), which was confirmed by our repeated experiments.

We first investigated the effect of O₂ pressure on the NH₃ conversion and N₂ selectivity of Cu/C, Ru/C and Ru–Cu/C catalysts. The temperature was kept at 150 °C and the performance of the catalysts over the change of O₂ pressure are shown in Fig. 1. 3Cu/C catalyst showed very poor activity for CWAQ of ammonia, where NH₃ conversion around 57% at 0.5 MPa. Although increase of O₂ pressure can enhance catalytic activity, the NH₃ conversion was still lower than 70% even if O₂ pressure was up to 2.0 MPa. The advantage of 3Cu/C catalyst is the excellent selectivity to nitrogen (~100%). Compared with 3Cu/C, the 3Ru/C catalyst showed higher NH₃ conversions at various O₂ pressure, the N₂ selectivity was however decreased from 90.5 to 85.8% when O₂ pressure was increased from 0.5 to 2.0 MPa. Clearly, combining Ru with Cu can remarkably improve the catalytic performance based on the results showed in Fig. 1. Although Ru loading was decreased to 1.5%, the 1.5Ru–1.5Cu/C bimetallic catalyst exhibited a 75% NH₃

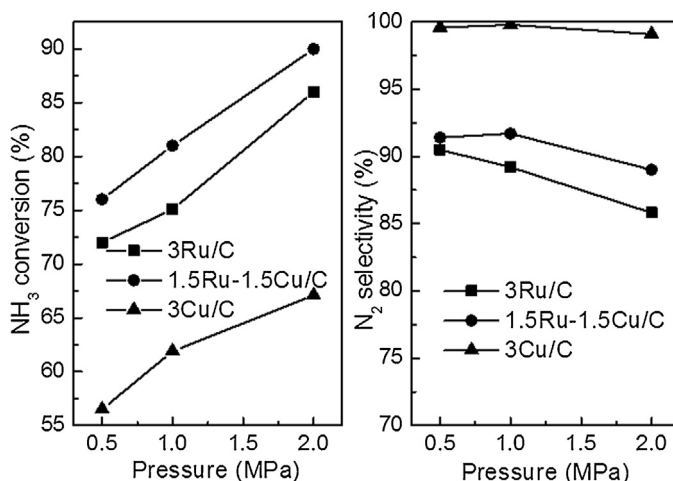


Fig. 1. Effect of oxygen pressure on catalytic performance of 3Ru/C (■), 1.5Ru–1.5Cu/C (●) and 3Cu/C (▲) catalysts. Conditions: 150 °C, pH 12, reaction time = 3 h.

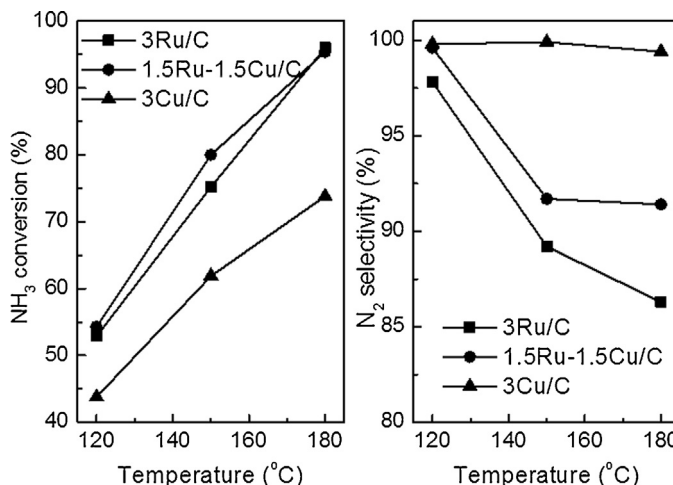


Fig. 2. Effect of reaction temperature on catalytic performance of 3Ru/C (■), 1.5Ru–1.5Cu/C (●) and 3Cu/C (▲) catalysts. Conditions: pH 12, oxygen pressure = 1 MPa, reaction time = 3 h.

conversion at 0.5 MPa which was higher than that of 3Cu/C catalyst at 2.0 MPa and 3Ru/C catalyst at 1.0 MPa. When O₂ pressure was increased to 2.0 MPa, NH₃ conversion could reach to 90.0% for 1.5Ru–1.5Cu/C bimetallic catalyst. Except for the highest activity, 1.5Ru–1.5Cu/C bimetallic catalyst also possessed better selectivity than Ru/C catalyst in the whole range of testing pressure while worse than 3Cu/C catalyst. The synergetic effect between Ru and Cu makes 1.5Ru–1.5Cu/C bimetallic catalyst much more active and/or selective for CWAQ of ammonia compared to the two monometallic catalysts, 3Cu/C and 3Ru/C.

Fig. 2 illustrated the effect of temperature on the catalytic behaviors of 3Cu/C, 3Ru/C and 1.5Ru–1.5Cu/C catalysts, where the O₂ pressure was kept at 1.0 MPa. Synergetic effect on the catalytic performance is also observed in this case. Both high activity and reasonable selectivity were obtained over bimetallic catalyst. When temperature was increased from 120 to 180 °C, the NH₃ conversion for 1.5Ru–1.5Cu/C catalyst was increased from 54.3 to 95.4%. The Ru/C catalyst showed a comparable conversion with 1.5Ru–1.5Cu/C catalyst at these reaction temperatures, however, more undesirable product was formed and the selectivity to N₂ was only 86.3% at 180 °C. For Cu/C catalyst, only 73.8% of ammonia was decomposed even at 180 °C, although the temperature has a positive effect on

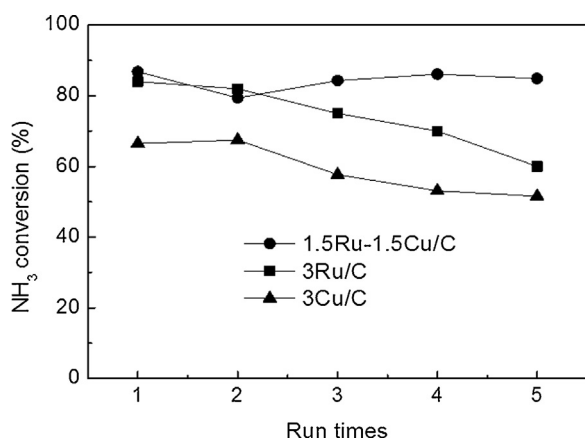


Fig. 3. Recycling experiments of 3Ru/C (■), 1.5Ru-1.5Cu/C (●) and 3Cu/C (▲) catalysts. Conditions: temperature = 150 °C, pH 12, oxygen pressure = 0.5 MPa, reaction time = 5.5 h.

the activity, while excellent selectivity was kept for Cu/C catalyst with the increase of reaction temperature.

The stability of catalyst is an important parameter in the practical application, perhaps more important than active CWAO of ammonia to nitrogen. Therefore, recycling operations were applied for utilized catalyst to examine the stability of 3Cu/C, 3Ru/C and 1.5Ru-1.5Cu/C catalysts at relative mild condition (150 °C and 0.5 MPa). After the first reaction run, the catalyst was recovered by filtration with deionized water and dried 12 h at 120 °C. To compensate the loss of catalyst, the first reaction run was repeated two times to ensure the use of the same amount catalyst (500 mg) in the recycling experiments. The conversion of ammonia after 5.5 h is given in Fig. 3 in the 5 recycling experiments. As can be seen, the two monometallic catalysts showed poor re-usability. The NH_3 conversion was decreased from 65 to 45% after 5 cycles over 3Cu/C catalyst and that was 85 to 65% over 3Ru/C catalyst. In contrast, the bimetallic catalyst, 1.5Ru-1.5Cu/C, exhibited an excellent stability, no deactivation was observed and the conversion of NH_3 was maintained at a level higher than 80% in the 5 consecutive runs. This observation indicates that the synergetic effect between Ru and Cu not only results in high activity but also leads to good stability.

Furthermore, the synergetic effect between Ru and Cu could help to keep the surface area of the catalyst. For the fresh 1.5Ru-1.5Cu/C, the surface area based on BET was 1277 cm^2/g . Although bit loss of BET surface area happened after the first run reaction, the surface area was almost constant (about 1040 cm^2/g) during the following runs. These was consistent with the stable activity of catalyst as shown in Fig. 3.

3.2. Characterization of carbon supports and supported catalysts

To clarify the synergetic effect between Ru and Cu, various characteristic analysts were carried out for 3Cu/C, 3Ru/C and 1.5Ru-1.5Cu/C catalysts. Firstly, X-ray diffraction (XRD) was used to analyze the crystal structure of the prepared catalysts, as shown in Fig. 4 and XRD pattern obtained from C support was also shown for comparison. Typical diffraction peaks due to the metallic Cu (1 1 1), Cu (2 0 0) planes were observed in 3Cu/C while no diffraction peak attributed to Ru species was detected over 3Ru/C. This result suggested that Ru was dispersed on carbon black much better than copper. Over 3Cu/C catalyst, Cu_2O phase also was observed since Cu^0 could easily be oxidized into Cu^+ after exposure to air [24]. 1.5Ru-1.5Cu/C catalyst presented a very similar XRD pattern with the C support. Even Cu loading was increased to 3 wt%, no phase belong to Cu species can be observed. The possible reason is that

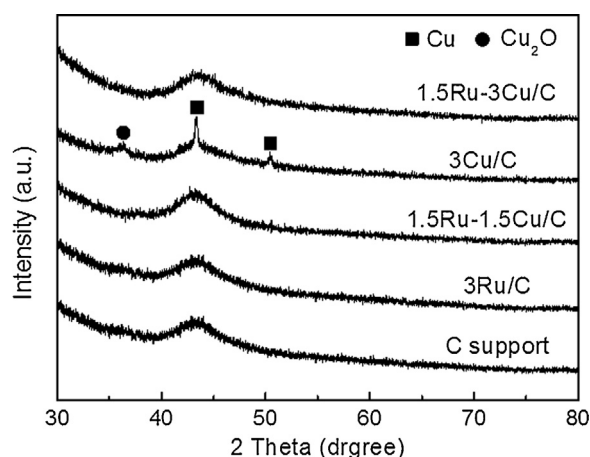


Fig. 4. XRD patterns of different samples.

the strong interaction between Ru and Cu, as confirmed by XPS and H_2 -TPR results later, can effectively promote the dispersion of Cu.

Fig. 5 was the transmission electron microscope (TEM) images of the supported catalysts. For 3Cu/C catalyst, Cu metal was poorly dispersed and aggregated into large particles (a mean diameter of 8.2 nm), while Ru metal had better dispersion over the 3Ru/C catalyst with an average size of 4.0 nm even though a bit large size distribution. For 1.5Ru-1.5Cu/C bimetallic catalysts, the average size of metal particles was also 4.3 nm and highly dispersed with narrow size distribution. These results are consistent with XRD patterns which confirm the effect of Ru on the metal particles dispersion.

XPS characterizations were conducted to investigate the surface chemical state of 3Cu/C, 3Ru/C and 1.5Ru-1.5Cu/C catalysts. The most intensive photoemission line of Ru 3d_{5/2} is overlapped with C 1s line from carbon support. Therefore, the Ru surface species were investigated by analyzing the Ru 3p_{3/2} line. The results are shown in Fig. 6. As can be seen, the binding energy of Ru in 3Ru/C catalyst was observed at 463.2 eV while that in Ru-Cu/C bimetallic catalyst was at 461.8 eV. Binding energy shifting a lower value implies that there exists a strong interaction between Ru and Cu and some electrons are transferred from Cu to Ru. The interaction and electron transfer between Ru and Cu are further confirmed by the XPS results of Cu 2p_{3/2}. In Cu/C catalyst, the binding energy of Cu centered at 932.6 eV, whereas, in Ru-Cu/C bimetallic catalyst, it was shifted to 932.9 eV due to the fact that some electrons were transferred to Ru. Jiang et al. also observed the strong interaction and electron transfers between Ru and Cu over a Ru-Cu bimetallic catalyst. However, the binding energies of both Ru and Cu were shifted to higher values in their work [25].

The redox property of oxygen species over 3Cu/C, 3Ru/C and 1.5Ru-1.5Cu/C catalysts was investigated by H_2 -TPR experiments, since it was a very essential both for NH_3 conversion and N_2 selectivity. Prior to H_2 -TPR experiment, the sample was treated by O_2 at 150 °C for 2 h to generate oxygen species. As shown in Fig. 7, 3Cu/C catalyst presented a main reduction peak at 281 °C with a shoulder peak at 221 °C, and H_2 consumption was extended to a temperature up to 340 °C, indicating that the reactivity of oxygen species over 3Cu/C is much lower. For 3Ru/C catalyst, the main reduction peak was at 168 °C and no H_2 consumption peak was observed at temperatures higher than 250 °C. These results suggest that the oxygen species over 3Ru/C catalyst possesses a relative high reactivity. Over 1.5Ru-1.5Cu/C bimetallic catalyst, the oxygen species exhibited a moderate reactivity and the main reduction peak was at 230 °C, very closed to the average value of those of 3Cu/C and 3Ru/C. Obviously, the co-existing of Ru and Cu can effectively tune the reactivity of oxygen species over catalyst surface. Except for reactivity,

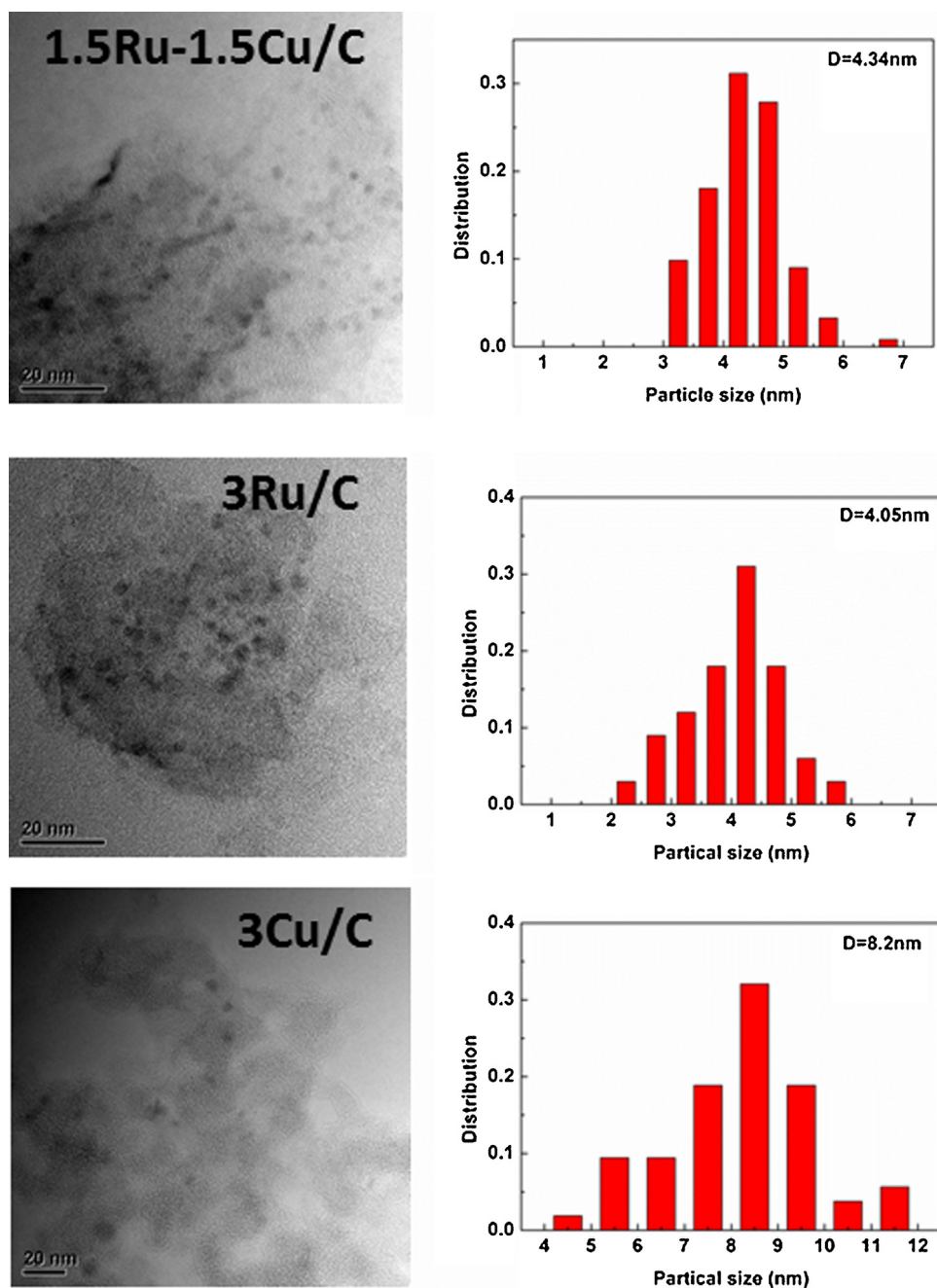


Fig. 5. TEM images of 3Cu/C, 3Ru/C and 1.5Ru-1.5Cu/C.

coverage of oxygen species also can be adjusted by the co-presence of Ru and Cu. It can be clearly seen that the area of H_2 consumption peak over 1.5Ru-1.5Cu/C is much higher than that over 3Ru/C. Mild activity and proper coverage of oxygen species are probable reasons to enhance the catalytic performance for CWAQ to N_2 over the bimetallic catalyst.

The leaching of active metal during reaction is a common problem that results in the deactivation of CWAQ catalyst. The catalysts after reaction test were analyzed by ICP-MS to study the leaching of Cu, Ru and the results were listed in Table 2, where the fresh catalysts were also included for comparison. It can be seen that, Ru and Cu loading decreased with the reaction proceeding over Ru/C and Cu/C catalysts respectively, indicating the leaching took place during the CWAQ process for these two catalysts. Certainly, such

Table 2

Metal leaching from the solid upon reaction as measured by ICP-MS analysis of the final treated effluents after oxidation of ammonia at 150 °C and 0.5 MPa.

Catalyst	Cycle	% Ru leached	% Cu leached
1.5Ru-1.5Cu/C	1	Undetected	Undetected
1.5Ru-1.5Cu/C	2	Undetected	Undetected
1.5Ru-1.5Cu/C	3	Undetected	Undetected
3Cu/C	1	/	2.16
3Cu/C	2	/	1.96
3Cu/C	3	/	0.52
3Ru/C	1	4.7	/
3Ru/C	2	3.3	/
3Ru/C	3	5.8	/

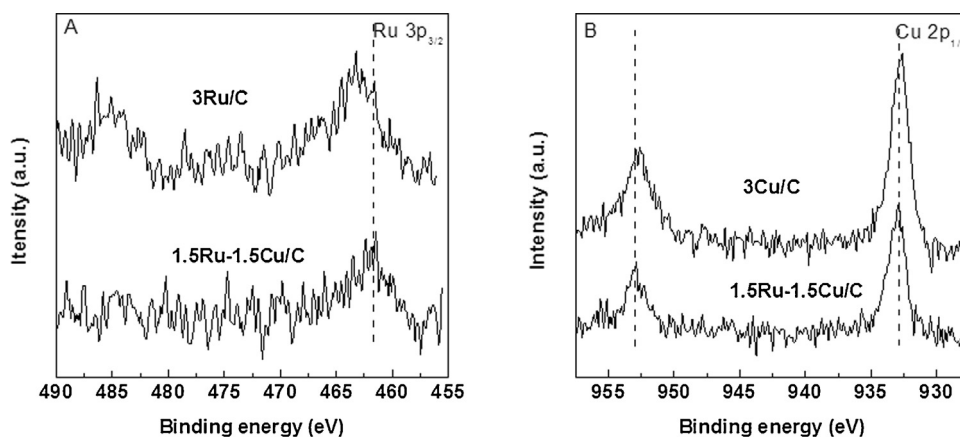


Fig. 6. XPS results of 3Ru/C, 1.5Ru-1.5Cu/C and 3Cu/C catalysts. A: Ru 3p_{3/2} and B: Cu 2p_{1/2}.

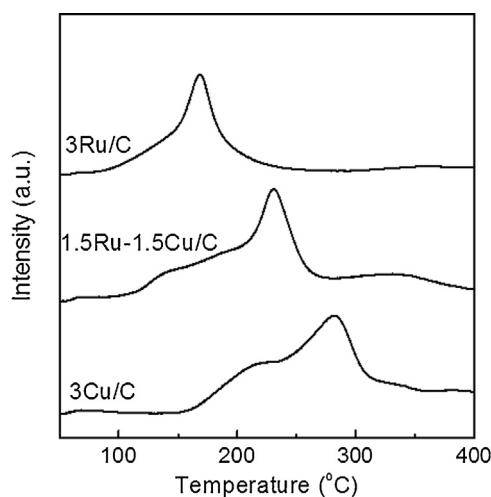


Fig. 7. H₂-TPR profiles of 3Ru/C, 1.5Ru-1.5Cu/C and 3Cu/C catalysts.

leaching resulted in the loss of active metal and the deactivation of Ru/C and Cu/C catalysts. The 1.5Ru-1.5Cu/C catalyst exhibited very excellent ability against leaching and even after 3 cycles, the used catalyst presented the same metal loadings as those of fresh catalyst. The possible reason is that the strong interaction between Ru and Cu can effectively prevent Ru and Cu eluting from catalyst and thus remarkably improve the catalytic stability, as shown in Fig. 3.

In order to study the relationship between the properties of oxygen species and the catalytic behavior of CWA/O catalyst, the variation of the main reduction peak with composition of the prepared catalysts with the same total loading of 3 wt% is plotted in Fig. 8, accompanied by NH₃ conversion and N₂ selectivity. It can be seen that N₂ selectivity increased from 85.8 to 99.1% when the main reduction temperature increased from 168 to 282 °C, indicating the reactivity of oxygen species plays a very important role in affecting the selectivity. Higher reactivity results in the formation of un-desirable by product while lower reactivity favors the production of N₂. NH₃ conversion shows a volcano shape with variation of main reduction temperature, which can be explained by the balance between the reactivity and the coverage of oxygen. Since NH₃ is activated over surface oxygen, 3Ru/C catalyst showed a relative high NH₃ conversion due to the high reactivity of oxygen. However, the amount of oxygen may be not enough for NH₃ activation due to the low oxygen affinity of Ru. The H₂-TPR results also indicated that 3Ru/C catalyst presented less H₂ consumption compared with 1.5Ru-1.5Cu/C catalyst. Increasing the O₂ pressure can increase the population of oxygen, thus NH₃ conversion increased from 72.0 to

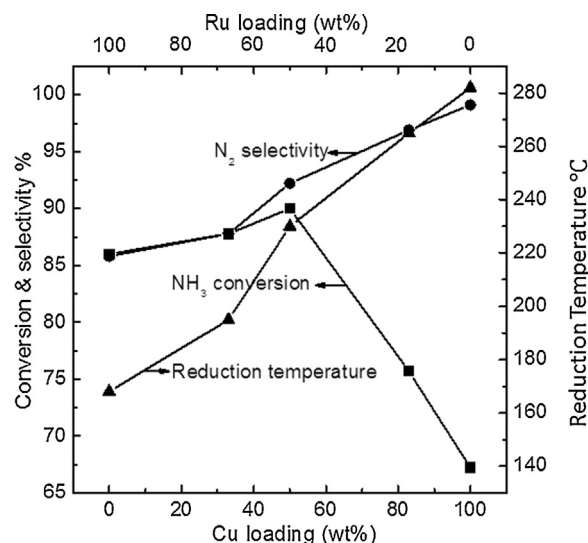


Fig. 8. Variations of main reduction peak and catalytic performance as function of composition of catalyst. Reaction conditions: 150 °C, pH 12, reaction time = 3 h.

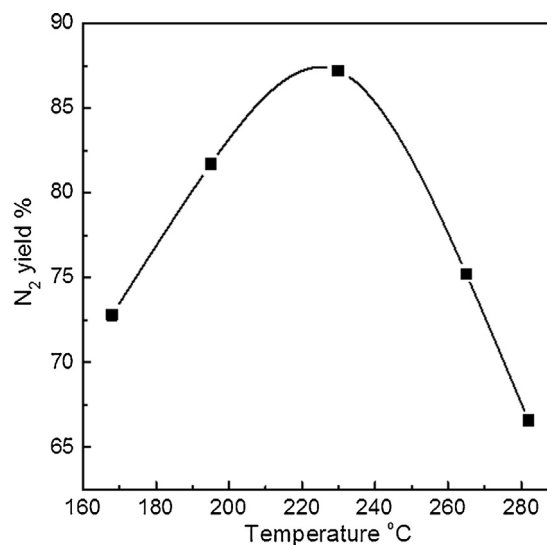


Fig. 9. Effect of main reduction temperature on the N₂ yield. Reaction conditions: 150 °C, pH 12, reaction time = 3 h. The data are taken from Fig. 8.

86.0% when O₂ pressure raised from 0.5 to 2.0 MPa, while the N₂ selectivity was decreased due to the high coverage and reactivity of oxygen. H₂-TPR results also indicated that the presence of Cu could enhance the oxygen affinity of Ru. Therefore, the NH₃ conversion firstly increased with the increasing of Cu due to the increasing amount of active oxygen over catalyst. However, when Cu loading was beyond 1.5 wt%, the main reduction temperature was shifted to a value higher than 250 °C. The low reactivity of oxygen resulted in the decrease of NH₃ conversion with further increasing Cu amount. Clearly, both the moderate reactivity and proper coverage of oxygen were the critical factors that determine the removal efficiency of NH₃ in wastewater, as shown in Fig. 9.

4. Conclusion

The results of this study demonstrated that Ru–Cu/C bimetallic catalyst was much more effective and stable for CWAQ of aqueous ammonia to N₂ compared with the two corresponding mono-metallic catalysts, Ru/C and Cu/C. The bimetallic catalyst possesses high activity, selectivity and stability at relative mild conditions. On the other hand, Ru/C catalyst shows high activity but low selectivity whereas Cu/C catalyst high selectivity but low activity. The two mono-metallic catalysts also suffer deactivation mainly due to the leaching of active metal. Over Ru–Cu/C bimetallic catalyst, the co-existing of Ru and Cu can effectively tune the reactivity and converge of oxygen species and suppress the leaching of Ru and Cu due to the strong the interaction between Ru and Cu. These can be related to excellent catalytic performance of Ru–Cu/C bimetallic catalyst.

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